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CHEMICAL ANALYSIS OF AEROSOL IN THE VENUSIAN CLOUD LAYER BY
REACTION GAS CHROMATOGRAPHY ON BOARD THE VEGA LANDERS

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16. Abstract The experiment on sulfuric acid aerosol determination in the Venusian cloud layer on board the Vega landers is described. An average content of sulfuric acid of $\sim 1 \text{ mg/m}^3$ was found for the samples taken from the atmosphere at heights from 63 to 48 km and analyzed with the SIGMA-3 chromatograph. Sulfur dioxide SO_2 was revealed in the gaseous sample at the height of 48 km. From the experimental results and blank run measurements, a suggestion is made that the Venusian cloud layer aerosol consists of more complicated particles than the sulfuric acid water solution does.			
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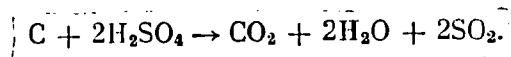
Investigations of the Venusian atmosphere by the method of gas /106*
chromatography (GC) which were conducted on the "Venera-12" (Gel'man
et al., 1979a,b), "Venera-13", "Venera-14" (Mukhin et al., 1982,
1983) and "Pioneer-Venera" (Oyama et al., 1980) landers made it pos-
sible to obtain data on the concentrations of the gaseous components.
However, analysis of the chemical composition of particles of the
cloud layer was not done with GC. It was considered (Young, 1973;
Knollenberg and Hunten, 1980) that these particles consist basically
of drops of sulfuric acid and correspond to a 75% concentration of
acid in water. In descriptions of physical-chemical processes which
occur in the upper part of the planet's atmosphere (Moroz, 1981), the
chemical composition of the aerosol plays an important role and in
this connection the assumption made required direct proof; this
determined the formulation of the experiment.

In order to solve the problem posed, a chromatographic informa- /107
tion measurement apparatus "Sigma-3" was developed. During its
development, several questions were resolved; the most important of
these were: investigating the chemical composition of the aéro-
sol, increasing the number of detectable components, increasing the
level of sensitivity while maintaining the reliability of the

* Numbers in the margin indicate pagination in the foreign text.

measurement apparatus. In the analytical part of the device were universal detectors (helium and katharometer) and selective detectors (electron capture - ECD). The katharometer in the domestic chromatograph was used for the first time in interplanetary investigations in order to increase the dynamic range of the measurements. The introduction of various types of detectors, three blocks of reaction cells and two independent analytical channels (gas-carriers - nitrogen and helium) into the device significantly broadened the potentials of the chromatographic experiment. Thermoreaction cells were equipped with a fiberglass filter coated with carbon. The channel with the helium detector and katharometer was intended for studying atmospheric components and products of the reaction of carbon with sulfuric acid from two thermoreaction cells. From a third thermoreaction cell along another analytical channel equipped with ECD and consisting of two chromatographic columns connected in parallel (the columns are filled with various sorbents), it is proposed to obtain information on the concentrations of oxygen, haloid and sulfur compounds and products of the reaction mentioned. Thus, the reliability of identifying the components being determined was increased.

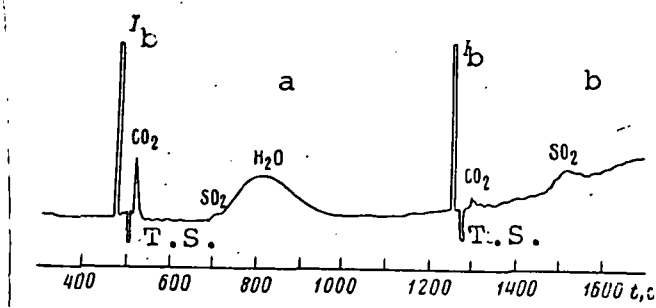
It is possible to do a quantitative analysis of sulfuric acid after determining the volumes of gases released as a result of the reaction:



An investigation of this reaction by the method of reaction gas chromatography showed (Porshnev and Bondarev, 1984) that the use of the method of the preliminary accumulation of H_2SO_4 aerosol on the fiberglass filter coated with carbon and the subsequent running of the reaction at elevated temperatures make it possible to do quantitative measurements at the level of 10^{-3} g with an error of approximately 10%. However, since in the planet's atmosphere CO_2 , H_2O and

SO₂ are present, in order to detect H₂SO₄ and measure its concentration, two stages of operation of the cells are envisioned. A known volume of atmosphere was pumped through the cells. Meanwhile, two of them were first heated to 80°C and the third cell was heated to 50°C as the vehicle landed. After sampling the cells were closed and for 30 s the gas sample was fed into the column with a flow of gas carrier. After the gas analysis, the third cell was heated to 80°C. Then in the second stage the hermetically sealed cell was heated to 300°C and the reaction products were supplied for analysis by a new switching of valves with the help of the gas carrier. Such a sequence of operations with the samples taken made it possible to separate sulfur dioxide as a reaction product from atmospheric SO₂. Information from the analytical channels on the temperatures of the thermostat of the columns and detectors, on the temperatures of the cells, on the operation of the cut-off devices, valves and suction device was transmitted telemetrically into digital and analog forms. /108

Identification of the maxima of the peak profiles on flight chromatograms was done according to the retention time of the components relative to the maximum of the peak profile of CO₂. The ratios of the components (c)/CO₂(c) obtained were compared with preliminary ground measurements. The quantitative interpretation of the results, as in the first case, was also done taking account of the real operating regime of the device while reproducing the flight conditions of chromatography. In addition, a cycle of idle measurements of "Sigma-3" was taken (without taking a sample, according to the standard program). From these chromatograms the possible level of contamination of the gas communications of the chromatograph and cells by terrestrial components during the storage of the device (the earth to Venus flight) was found. This made it possible to evaluate the operating sensitivity of the detectors, in particular the ECD. Examining the results of the experiment on the flight chromatograms after processing of the telemetric information and comparing them with ground control measurements made it possible to identify and determine quantitatively H₂SO₄ in the form of aerosol



Chromatograms of the separation of samples of the Venusian cloud layer (column 54 cm long, filled with Porapak T, gas carrier - nitrogen, electron capture detector, temperature 82°C). a - sample of atmospheric gas taken at an altitude of approximately 48 km, b - sample of aerosol from the cloud layer, taken in the range of altitudes from 63 to 48 km. I_b - background current of the detector, T.S. - electrical test-signal

in the cloud layer of Venus (figure). Starting from the volume of atmosphere pumped through the cell (0.07 m³), 100% effectiveness of recovery and retention of sulfuric acid aerosol by the filter, completeness of running its reaction with carbon, we found that in the sample taken at the range of altitudes from 63 to 48 km, the average H₂SO₄ concentration was ~1 mg/m³. In the gas sample of atmosphere at altitude 48 km, sulfur dioxide was identified (figure). We must note that in the process of analyzing gas samples from 48 km and especially the integral sample

of aerosol at altitudes from 63 to 48 km, a sharp drop was observed in the sensitivity of the helium and electron capture detectors, along with drift of the zero line of the informing devices. The reproduction of chromatography conditions and the detected level of contamination of the analytical part of the device still do not make it possible to explain the reasons for anomalies in the behavior of the detectors and the shift in the zero line. This circumstance makes it possible to propose that the cloud layer may consist of particles of more complex composition than an aqueous sulfuric acid solution. In this case in thermoreaction cells at elevated temperatures, in addition to reaction $C + H_2SO_4$, there may be more complex processes, including dissociation of the sample.

Supplementing and refining the results obtained will require model experiments which consider the role of both instrument

factors and the chemical activity of the materials being studied.

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